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I, Kenji Ohdan, state:

that I am thoroughly familiar with both the Japanese and English languages; and

that the attached document represents a true English translation of the Japanese Application No. 10-235453.

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Date

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Translator



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Applicant:	TOKYO OHKA KOGYO CO., LTD.

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using the same
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【Name of document】 Specification

【Title of the invention】 Positive-working resist composition and resist pattern-forming method by using the same

【The claims】

【Claim 1】 A positive-working resist composition characterized in that an oxoacid of phosphorus or a derivative thereof is added to a radiation-sensitive positive-working resist containing a combination of a resinous ingredient capable of being imparted with increased solubility in an alkaline aqueous solution by interaction with an acid and an acid-generating ingredient generating an acid by irradiation of a radiation.

【Claim 2】 The positive-working resist composition described in Claim 1 in which the adding amount of the oxoacid of phosphorus or derivative thereof is 0.01 to 5% by weight based on the weight of the resinous ingredient.

【Claim 3】 The positive-working resist composition described in Claim 1 or 2 in which the oxoacid of phosphorus or derivative thereof is at least one kind selected from phosphoric acid, phosphorus acid, phosphonic acid, phosphinic acid and esters thereof.

【Claim 4】 The positive-working resist composition described in Claim 1, 2 or 3 in which the acid-generating ingredient is an onium salt with a fluoroalkyl sulfonate as the anion.

【Claim 5】 The positive-working resist composition described in either one of Claims 1 to 4 in which the resinous ingredient is a copolymer containing ester units of acrylic acid or methacrylic acid having acid-dissociable solubility-reducing groups.

【Claim 6】 The positive-working resist composition described in Claim 5 in which the copolymer containing ester units of acrylic acid or methacrylic acid having acid-dissociable solubility-reducing groups is a copolymer consisting of 50 to 85% by moles of hydroxystyrene units, 10 to 30% by moles of styrene units and 2 to 20% by moles of tertiary alkyl acrylate or tertiary alkyl methacrylate units.

【Claim 7】 A resist pattern-forming method characterized in that, in a resist pattern-forming method in which a coating film of a positive-working resist composition is provided on a substrate provided with a thin film and the said coating film is light-exposed through a mask pattern followed by heating and then by a development treatment, a positive-working resist composition containing a combination of a resinous ingredient capable of being imparted with increased solubility in an alkaline aqueous solution by interaction with an acid and an acid-generating ingredient generating an acid by irradiation with a radiation and also containing an oxoacid of phosphorus or a derivative thereof is used as the positive-working resist composition.

【Claim 8】 The method described in Claim 7 in which the thin film is a thin film containing nitrogen or a thin film containing at least one of phosphorus and boron.

【Claim 9】 The method described in Claim 8 in which the nitrogen-containing thin film is a thin film of a nitride selected from monosilicon mononitride (SiN), trisilicon tetranitride (Si_3N_4), silicon oxynitride (SiON) and titanium nitride (TiN).

【Claim 10】 The method described in Claim 8 in which the thin film containing at least one of phosphorus and boron is a thin film of glass selected from phosphosilicate glass, borosilicate glass and boro-phosphosilicate glass.

【Detailed description of the invention】

【0001】

【Technological field to which the invention belongs】

The present invention relates to a chemical-amplification positive-working resist composition suitable for a lithographic process by using a fine resist pattern of $0.2\ \mu\text{m}$ or finer, which is excellent in the sensitivity and pattern resolution and capable of forming a resist pattern having orthogonality without skirt trailing and tapered form in the cross section onto substrates provided with a variety of thin films as well as to a method for the formation of a resist pattern by the use of this composition.

[0002]

[Prior art technology]

While, in recent years, practical use is attempted of a lithographic process requiring pattern resolution of around 0.25 μm by using a chemical-amplification resist, for example, a chemical-amplification positive-working resist, the requirement for fineness of semiconductor devices is increasing more and more so that development is now under way for semiconductor devices requiring fineness of 0.20 μm or finer.

[0003]

The chemical-amplification resist is a resist by utilizing the catalytic activity of an acid formed by irradiation with a radiation and has advantages that the sensitivity and pattern resolution are high and the used amount of the compound to generate an acid by the irradiation with a radiation, i.e. acid-generating agent, can be small.

Chemical-amplification resists include two types of positive-working and negative-working ones and the base components thereof in general are an acid-generating agent and a film-forming ingredient which is subject to a change of the solubility in an alkaline aqueous solution by the interaction of the generated acid.

[0004]

In the aforementioned positive-working resist, the film-forming ingredient to be used is usually a polyhydroxystyrene, a copolymer thereof and the like of which a part of the hydroxyl groups are protected with solubility-reducing groups such as *tert*-butoxycarbonyl groups, tetrahydropyranyl groups and the like.

[0005]

In the semiconductor devices, meanwhile, it is usual to use, as the substrate, those provided with a thin film of a great variety of kinds having various functions on a silicon wafer. For example, phosphorus-containing thin films of phosphosilicate glass (PSG), boron-containing thin films of borosilicate glass (BSG), boron- and phosphorus-containing thin films of boro-phosphosilicate glass (BPSG) and silicon

nitride-based thin films of SiON, SiN, Si₃N₄ and the like are provided as an interlayer insulation film or circuit wiring-protective film and a semiconductor thin film of polycrystalline silicon (poly-Si) is provided as a gate electrode or resistance. Further, metal-based thin films of aluminum, aluminum-silicon-copper alloys, titanium nitride, tungsten, titanium-tungsten alloys and the like are provided as an electrode or circuit wiring.

【0006】

While, in the manufacture of semiconductor devices, a resist pattern is formed on a substrate provided with such a great variety of thin films by the lithographic process, a small trailing skirt is found at the interface with the thin film in the cross section of the resist pattern when a resist pattern is formed on a substrate provided, for example, with the aforementioned nitrogen-containing thin film such as silicon nitride-based thin films, TiN thin films and the like by using a chemical-amplification positive-working resist. When a resist pattern is formed on a substrate provided with a PSG film, BSG film or BPSG film, furthermore, it is usually unavoidable that the cross section is in a somewhat tapered form.

And, if such skirt trailing occurs or a tapered form is resulted in the lithographic process in which a fine resist pattern of 0.20 μm or finer is required, a serious drawback may be encountered in the succeeding steps so that improvement in this regard is strongly desired.

【0007】

【Problems to be solved by the invention】

Under these circumstances, the present invention has been completed with an object to provide a chemical-amplification positive-working resist composition having excellent sensitivity and pattern resolution and capable of forming a resist pattern of orthogonal cross section free from trailing skirts and tapered form in the cross section on a substrate provided with a variety of thin films to be suitable for a lithographic process using a fine resist pattern of 0.2 μm or finer.

[0008]

[Means to solve the problems]

The inventors have continued extensive investigations to develop a chemical-amplification positive-working resist composition exhibiting excellent performance and, as a result, have arrived at a discovery that, directing their attention to the fact that the cause for the occurrence of skirt trailing or tapered profile when a resist pattern is formed by using a chemical-amplification positive-working resist on a substrate provided with a variety of thin films is coupling of the acid generated from the acid-generating agent with the non-covalent electron pair possessed by the atoms such as nitrogen, phosphorus, boron and the like in the said thin film leading to deactivation of the acid, the object can be accomplished by preventing deactivation of the aforementioned acid when an oxoacid of phosphorus or a derivative thereof is added to the chemical-amplification positive-working resist leading to completion of the present invention on the base of this discovery.

[0009]

Namely, the present invention provides a positive-working resist composition characterized in that an oxoacid of phosphorus or a derivative thereof is added to a radiation-sensitive positive-working resist containing a combination of a resinous ingredient capable of being imparted with increased solubility in an alkaline aqueous solution by interaction with an acid and an acid-generating ingredient generating an acid by irradiation of a radiation and a method for the formation of a resist pattern characterized in that a coating film of the above mentioned positive-working resist composition is formed on a substrate provided with a thin film, which is light-exposed through a mask pattern followed by heating and then by a development treatment.

[0010]

[Practicing mode of the invention]

The resinous ingredient capable of being imparted with increased solubility in an alkaline aqueous solution by the

interaction of an acid to be used in the positive-working resist composition of the present invention can be used by appropriately selecting from known resins used in prior art chemical-amplification positive-working resists such as, for example, those resins of which the phenolic hydroxyl groups or hydroxyl groups of carboxyl groups in an alkali-soluble resin are protected by acid-dissociable solubility-reducing groups. Such a resin is rendered alkali-insoluble when the above mentioned hydroxyl groups are protected by acid-dissociable solubility-reducing groups but rendered alkali-soluble when the said solubility-reducing groups are dissociated by the interaction of the acid formed from the acid-generating agent resulting in an increase in the solubility in an alkaline aqueous solution.

[0011]

The acid-dissociable solubility-reducing group used here can be any one freely selected from those heretofore known groups of this kind. Such a group is exemplified, for example, by tertiary alkyloxycarbonyl groups such as *tert*-butoxycarbonyl group, *tert*-amyloxycarbonyl group and the like, tertiary alkyl groups such as *tert*-butyl group, *tert*-amyl group and the like, tertiary alkyloxycarbonylalkyl groups such as *tert*-butoxycarbonylmethyl group, *tert*-amyloxycarbonylmethyl group and the like, cyclic acetal residues such as tetrahydropyranyl group, tetrahydrofuranyl group and the like, chained acetal residues such as alkoxyalkyl group and the like, silyl ether groups such as trimethylsilyl group, and so on.

Among them, tertiary alkyloxycarbonyl groups, tertiary alkyl groups, cyclic acetal residues and chained acetal residues are particularly preferable due to the excellent sensitivity, pattern resolution and resist pattern profile.

[0012]

Such a resin protected with acid-dissociable solubility-reducing groups is exemplified, for example, by (a) a polyhydroxystyrene in which from 10 to 50% by moles or, preferably, from 15 to 35% by moles of the hydroxyl groups are protected

with *tert*-butoxycarbonyl groups, (b) a polyhydroxystyrene in which from 10 to 50% by moles or, preferably, from 15 to 35% by moles of the hydroxyl groups are protected with *tert*-butoxycarbonylmethyl groups, (c) a polyhydroxystyrene in which from 10 to 50% by moles or, preferably, from 15 to 35% by moles of the hydroxyl groups are protected with cyclic acetal residues such as tetrahydropyranyl groups, tetrahydrofuranyl groups and the like, (d) a polyhydroxy-styrene in which from 10 to 50% by moles or, preferably, from 15 to 35% by moles of the hydroxyl groups are protected with alkoxyalkyl groups including chained acetal residues such as 1-ethoxyethyl groups, 1-methoxy-*n*-propyl groups and the like, and (e) a copolymer consisting of from 50 to 85% by moles of hydroxystyrene units, from 10 to 30% by moles of styrene units and from 2 to 20% by moles of acrylic acid or methacrylic acid ester units having acid-dissociable solubility-reducing groups or, preferably, *tert*-butyl group. The hydroxystyrene unit in this (e) implied here is a unit derived from a hydroxystyrene or α -methyl hydroxystyrene or both.

[0013]

These resinous ingredients can be used singly or can be used as a combination of two kinds or more. Inter alia, a combination of the aforementioned (a) and (d) and a combination of the (c) and (d) or, in particular, those of (e) alone are satisfactory due to excellent resist pattern profile and pattern resolution as well as small edge roughness (unevenness of resist pattern-top edge portions when the resist pattern is observed from just above). As to the using proportion when a combination is used, the weight proportion of the resin (a) or (c) and the resin (d) should better be selected from 5:95 to 50:50 or, preferably, from 10:90 to 30:70. As to that of the (e) alone, it can be a mixture of two kinds or more of resins with different % molar fractions of the respective units provided that the % molar fractions of the respective units in (e) are satisfied.

[0014]

As to the acid-generating ingredient capable of

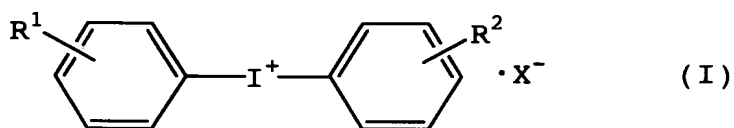
generating an acid by the irradiation with a radiation to be used in the inventive composition, on the other hand, while various kinds of known acid-generating ingredients under use in conventional chemical-amplification resists can be used, onium salts and diazomethane compounds are preferable in respects of the strength of the generated acid, dissociability of the solubility-reducing groups in the aforementioned resinous ingredient, transparency to the light for light-exposure and so on.

The diazomethane compound is exemplified, for example, by bis(cyclohexylsulfonyl)diazomethane, bis(*tert*-butylsulfonyl)diazomethane, bis(isopropylsulfonyl)diazomethane, bis(4-methylphenylsulfonyl)diazomethane and bis(2,4-dimethylphenylsulfonyl)diazomethane.

[0015]

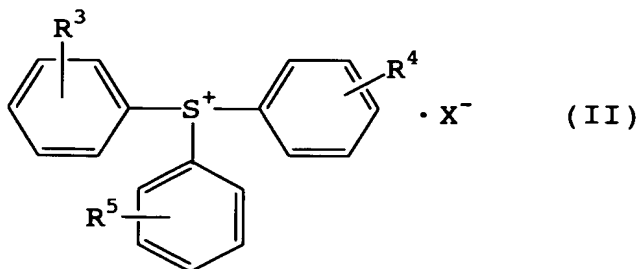
As the onium salt, the onium salts having a fluoroalkyl sulfonate as the anion including the diphenyliodonium salts represented by the general formula

[Chem 1]



(R^1 and R^2 in the formula are each a hydrogen atom, an alkyl group of 1 to 4 carbon atoms or an alkoxy group of 1 to 4 carbon atoms, which can be the same to the other or can be different from the other, and X^- is a fluoroalkylsulfonic acid ion of 1 to 10 carbon atoms), and the triphenylsulfonium salts represented by the general formula

[Chem 2]



(R³, R⁴ and R⁵ in the formula are each a hydrogen atom, an alkyl group of 1 to 4 carbon atoms or an alkoxy group of 1 to 4 carbon atoms, which can be the same as the others or can be different from the others, and X⁻ has the same meaning as mentioned before) are particularly preferable.

【0016】

Examples of the onium salts represented by the above given general formulas (I) and (II) include diphenyliodonium trifluoromethanesulfonate or nonafluorobutanesulfonate, bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate or nonafluorobutanesulfonate, triphenylsulfonium trifluoromethanesulfonate or nonafluorobutanesulfonate, tri(4-methylphenyl)sulfonium trifluoromethanesulfonate or nonafluorobutanesulfonate and the like, of which methanesulfonate or nonafluorobutanesulfonate of bis(4-*tert*-butylphenyl)iodonium and triphenylsulfonium are particularly preferable because of the good resist pattern profile and pattern resolution.

【0017】

In the present invention, these acid-generating ingredients can be used singly or can be used as a combination of two kinds or more. The compounding amount thereof is selected usually in the range from 1 to 10 parts by weight per 100 parts by weight of the above-mentioned resinous ingredient. When this amount is smaller than 1 part by weight, image formation can hardly be accomplished while, when 10 parts by weight is exceeded, difficulties are encountered in obtaining a uniform solution to cause a decrease in the storage stability.

【0018】

In the positive-working resist of the present invention, it is essential that an oxoacid of phosphorus or a derivative thereof is further added to the combination of the aforementioned resinous ingredient and the acid-generating ingredient.

When a resist pattern is formed by using the chemical-amplification resist on a substrate provided with a thin film including nitrogen-containing thin films such as silicon nitride-based thin films of SiN, Si₃N₄, SiON and the like and

thin films of TiN, phosphorus-containing thin films of PSG films and the like, boron-containing thin films of BSG films and the like and phosphorus- and boron-containing thin films of BPSG films and the like, it is sometimes the case that the cross section has trailing skirts or the cross section is in a tapered form. The reason therefor is presumably that the non-covalent electron pair possessed by the atoms of nitrogen, phosphorus, boron and the like in the aforementioned thin film and the acid generated from the acid-generating agent are combined together resulting in deactivation of the acid. Accordingly, the aforementioned deactivation of the acid can be effectively prevented by the admixture of an oxoacid of phosphorus or a derivative thereof without adversely influencing the sensitivity and pattern resolution.

[0019]

Examples of the oxoacid of phosphorus and derivatives thereof include phosphoric acid, phosphorus acid and derivatives thereof, e.g., esters such as phosphoric acid, phosphorous acid, di-n-butyl phosphate, diphenyl phosphate and the like, phosphonic acid and derivatives thereof, e.g., esters such as phosphonic acid, dimethyl phosphonate, di-n-butyl phosphonate, phenyl phosphonate, diphenyl phosphonate, dibenzyl phosphonate and the like and phosphinic acid and derivatives thereof, e.g., esters such as phosphinic acid, phenyl phosphinic acid and the like, and others.

[0020]

These oxoacids of phosphorus and derivatives thereof can be used singly or can be used as a combination of two kinds or more. The amount of addition thereof is preferably in the range from 0.01 to 5% by weight based on the weight of the aforementioned resinous ingredient. When this amount is smaller than 0.01% by weight, the improving effect on the skirt trailing and tapered form in the cross section of the resist pattern cannot be fully exhibited while, when in excess over 5% by weight, the resist pattern suffers occurrence of film reduction. In respect of the improving effect on skirt trailing and tapered form and suppression of film reduction of

the resist pattern, a more preferable amount of addition of the oxoacid of phosphorus or a derivative thereof is in the range from 0.1 to 2.0% by weight.

【0021】

It is optional that the positive-working resist composition of the present invention can further be admixed according to need with a quencher such as secondary or tertiary amines such as triethylamine, tributylamine, dibutylamine, triethanolamine and the like and an antireflection agent to prevent reflection from the substrate such as benzophenone and the like.

【0022】

It is preferable that the composition of the present invention, in the use thereof, is used in the form of a solution by dissolving the above described various ingredients in a solvent. Examples of such a solvent include ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone, polyhydric alcohols and derivatives thereof such as ethyleneglycol, ethyleneglycol monoacetate, diethyleneglycol, diethyleneglycol monoacetate, propyleneglycol, propyleneglycol monoacetate, dipropyleneglycol or dipropyleneglycol monoacetate as well as monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether or monophenyl ether thereof, cyclic ethers such as dioxane and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, ethyl ethoxypropionate and the like. They can be used singly or can be used as a mixture of two kinds or more.

【0023】

It is further optional according to desire that the composition of the present invention is admixed with and contains additives having miscibility such as, for example, auxiliary resins to improve the performance of the resist film, plasticizers, stabilizers, coloring agents, surface active agents and others under conventional use.

【0024】

In the resist pattern forming method of the present invention, in the next place, a substrate provided with a variety of thin films is provided with a coating film of the above described positive-working resist composition, which is light-exposed through a mask pattern followed by heating and then a development treatment thus to form a desired resist pattern.

【0025】

In the method of the present invention, it is preferable to use a substrate provided with a thin film containing nitrogen or a thin film containing at least one of phosphorus and boron. The thin film containing nitrogen here is exemplified by thin films of a nitride selected from monosilicon mononitride (SiN), trisilicon tetranitride (Si₃N₄), silicon oxynitride (SiON) and titanium nitride (TiN) and the thin film containing at least one of phosphorus and boron is exemplified by thin films of glass selected from phosphosilicate glass (PSG), borosilicate glass (BSG) and borophosphosilicate glass (BPSG).

【0026】

While the resist pattern forming method in the prior art resist technology can be used as the resist pattern forming method of the present invention, a satisfactory practice is that, firstly, a substrate such as a silicon wafer provided with a thin film as described above is coated with a solution of said resist composition on a spinner and the like followed by drying to form a coating film, which is irradiated with KrF excimer laser beams (248 nm) through a desired mask pattern, for example, on a KrF light-exposure machine and the like and drying. Nextly, the same is subjected to a development treatment by using a developer solution, e.g., an alkaline aqueous solution such as a 0.1 to 10% by weight aqueous solution of tetramethylammonium hydroxide. In this way, a resist pattern having fidelity to the mask pattern without occurrence of skirt trailing still with an orthogonal profile free from tapered form is formed. The resist pattern forming

method of the present invention is applicable also to the cases where X-rays or electron beams are used for the light source without being limited to KrF excimer laser beams.

【0027】

【Advantages of the invention】

The positive-working resist composition of the present invention is excellent in the sensitivity and pattern resolution and capable of forming a resist pattern having an orthogonal cross section free from skirt trailing without tapered form in the cross section on a substrate provided with a variety of thin films so that it can be used satisfactorily in a lithographic process for the use of a fine resist pattern of 0.2 μm or finer.

【0028】

【Examples】

In the following, the present invention is described in more detail by way of examples but the present invention is never limited by these examples in any way.

【0029】

Example 1.

A positive-working resist solution was prepared by dissolving, in 800 parts by weight of propyleneglycol monomethyl ether acetate, 60 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 65% by moles of hydroxystyrene units, 20% by moles of styrene units and 15% by moles of tert-butyl acrylate units, 40 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 65% by moles of hydroxystyrene units, 30% by moles of styrene units and 5% by moles of tert-butyl acrylate units, 5 parts by weight of triphenylsulfonium trifluoromethanesulfonate, 0.29 part by weight of phenylphosphonic acid and 0.27 part by weight of triethanolamine followed by filtration through a membrane filter of 0.2 μm pore diameter.

【0030】

In the next place, a 6-inch silicon wafer provided with a monosilicon mononitride (SiN) film was spin-coated with the

above described positive-working resist solution and dried on a hot plate at 130 °C for 90 seconds to form a resist layer of 0.7 μm film thickness. In the next place, selective irradiation was performed with KrF excimer laser beams on a minifying projection light-exposure machine FPA-3000EX3 (manufactured by Canon Co.) followed by a heat treatment at 110 °C for 90 seconds and then puddle development for 65 seconds in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide to obtain a positive-working resist pattern.

【0031】

In this way, a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing upright vertically on the substrate surface without skirt trailing. And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0032】

Example 2.

Resist patterning was conducted in the same manner as in Example 1 except that, in Example 1, the substrate was replaced with a 6-inch silicon wafer provided with a phosphosilicate glass (PSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0033】

Example 3.

Resist patterning was conducted in the same manner as in Example 1 except that, in Example 1, the substrate was replaced with a 6-inch silicon wafer provided with a borosilicate glass (BSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the

resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0034】

Example 4.

Resist patterning was conducted in the same manner as in Example 1 except that, in Example 1, the substrate was replaced with a 6-inch silicon wafer provided with a borophosphosilicate glass (BPSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0035】

Example 5.

A positive-working resist solution was prepared in the same manner as in Example 1 excepting, in Example 1, for the replacement of the phenylphosphonic acid with phosphoric acid and resist patterning was conducted on the substrate used in Example 1 in the same manner thereafter as in Example 1.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0036】

Example 6.

Resist patterning was conducted in the same manner as in Example 5 except that, in Example 5, the substrate was replaced with a 6-inch silicon wafer provided with a phosphosilicate glass (PSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the

resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0037】

Example 7.

Resist patterning was conducted in the same manner as in Example 5 except that, in Example 5, the substrate was replaced with a 6-inch silicon wafer provided with a borosilicate glass (BSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0038】

Example 8.

Resist patterning was conducted in the same manner as in Example 5 except that, in Example 5, the substrate was replaced with a 6-inch silicon wafer provided with a borophosphosilicate glass (BPSG) film.

The results were that a line-and-space pattern of 0.18 μm could be resolved and the cross sectional profile of the resist pattern was excellently orthogonal standing vertically on the substrate surface.

And, the minimum exposure dose to obtain the 0.18 μm resist pattern (sensitivity) was 40 mJ/cm².

【0039】

Comparative Example 1.

In Example 1, a positive-working resist composition with omission of phenylphosphonic acid was prepared and resist patterning was conducted in the same manner on the substrate used in Example 1.

The results were that, although a line-and-space pattern of 0.25 μm could be resolved, skirt trailing occurred in the cross sectional profile of the resist pattern.

And, the minimum exposure dose to obtain the 0.25 μm resist pattern (sensitivity) was 30 mJ/cm².

【0040】

Comparative Example 2.

A positive-working resist solution was prepared in the same manner as in Example 1 excepting, in Example 1, for the replacement of 0.29 part by weight of phenylphosphonic acid with 0.19 part by weight of malonic acid and resist patterning was conducted on the substrate used in Example 1 in the same manner.

The results were that, although a line-and-space pattern of 0.22 μm could be resolved, skirt trailing occurred in the cross sectional profile of the resist pattern.

And, the minimum exposure dose to obtain the 0.22 μm resist pattern (sensitivity) was 35 mJ/cm².

【0041】

Comparative Example 3.

A positive-working resist solution was prepared in the same manner as in Example 1 excepting, in Example 1, for the replacement of 0.29 part by weight of phenylphosphonic acid with 0.28 part by weight of p-toluenesulfonic acid and resist patterning was conducted on the substrate used in Example 1 in the same manner.

The results were that a semicircular resist pattern was found with a large film thickness reduction.

【0042】

Comparative Example 4.

In Example 1, a positive-working resist composition with omission of phenylphosphonic acid was prepared and resist patterning was conducted on the substrate used in Example 4 in the same manner.

The results were that, although a line-and-space pattern of 0.25 μm could be resolved, the cross sectional profile of the resist pattern was in a tapered form.

And, the minimum exposure dose to obtain the 0.25 μm resist pattern (sensitivity) was 30 mJ/cm².

【Name of document】 Abstract

【Abstract】

【Problems】 To provide a positive-working resist composition having excellent sensitivity and pattern resolution and capable of forming an orthogonal resist pattern without skirt trailing in the cross section on a substrate provided with a thin film as well as a resist pattern forming method by using the same.

【Means for solution】 A positive-working resist composition is formed by the addition of an oxoacid of phosphorus or a derivative thereof to a radiation-sensitive positive-working resist containing a combination of a resinous ingredient capable of being imparted with increased solubility in an alkaline aqueous solution by interaction with an acid and an acid-generating ingredient generating an acid by irradiation with a radiation.

And, a resist pattern is formed by providing a coating film of this composition on a substrate provided with a thin film and light-exposing the said coating film followed by heating and then a development treatment.

【Figure selected】 None

【Name of Document】 Office correction data
【Corrected document】 Application for patent

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